PATENT SPECIFICATION

(11) 1 303 773

NO DRAWINGS

(21) Application No. 26347/71 (22) Filed 19 April 1971

(31) Convention Application No. 26446 (32) Filed 7 April 1970 in

(33) United States of America (US)

(44) Complete Specification published 17 Jan. 1973

(51) International Classification C10M 3/42

(52) Index at acceptance

C5F 451 530 538 558 610 678 692 730 762 B

(19)

1303773

(54) TRACTIVE FLUIDS

(71) We, MONSANTO COMPANY, a corporation organised under the laws of the State of Delaware, United States of America, of 800 North Lindbergh Boulevard, St. Louis 66, State of Missouri, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to functional fluid compositions particularly adapted for use in tractive drives.

Traction is broadly defined as the adhesive friction of a body on a surface on which it moves. A tractive drive is a device in which torque is transmitted from an input element to an output element through nominal point or line contact, typically with a rolling action, by virtue of the traction between the contacting elements.

While tractive elements are commonly spoken of as being in contact, it is generally accepted that a fluid film is provided therebetween. Almost all tractive drives require fluids to remove heat, to prevent wear at the contact surfaces, and to lubricate bearings and other moving parts associated with the drive. Thus, instead of metal to metal rolling contact there is a film of fluid introduced into the load zone. The nature of this fluid determines to a large extent the limits in the performance and in the capacity of the drive. Desirable properties for a tractive fluid are (1) high coefficient of traction, (2) viscosity in the range of about 4 to 2000 centistokes over a temperature range of 210° F. to 0° F., (3) good oxidation resistance, (4) noncorrosive to common materials of construction and (5) good load-bearing and low wear rate properties.

A detailed discussion of tractive drives and fluid properties is given in British Patent Specification 1,190,836. This patent defines certain classes of fluids characterized by high coefficients of traction and preferred molecular structures, the use of which increases the torque capacity of tractive drives and permits a reduction in the size of the drive required for a given power requirement.

[*Price 25p*]

Although fluids of the type described in the aforesaid specification are among the best of any fluids known for tractive drives with respect to torque transmitting ability, for certain applications it would be desirable to improve their load-bearing capability and antiwear characteristics.

It is accordingly an object of the present invention to provide a superior tractive fluid having improved load-carrying capability and antiwear characteristics.

A composition of the present invention is one comprising (A) a major amount of a tractant base stock comprising an organic compound having a coefficient of traction of at least 0.06, and (B) an amount sufficient to improve the load-carrying capability of the base stock of a zinc di(neo - alkyl)phosphorodithioate wherein the neo - alkyl groups each contain from 5 to 13 carbon atoms. The addition of a minor amount of the zinc di(neo - alkyl)-phosphorodithioate to the base stock significantly increases the load-carrying capability of the fluid as measured by standard wear tests, without significantly diminishing the high temperature oxidation stability of the fluid as indicated by change in viscosity and corrosivity. A preferred additive is zinc di(neo - hexyl)-phosphorodithioate.

Typical tractive fluids useful in the present invention include those described at length in Specification No. 1,190,836. These fluids are defined in terms of certain structural units or elements present within their molecules which render the fluids particularly suitable for use in tractive devices. Suitable fluids include those organic compounds

(1) having from 12 to 70 carbon atoms, up to 8 of which can be replaced by atoms other than carbon atoms, which other atoms can, for example, be oxygen, nitrogen, phosphorus or silicon atoms, and

(2) containing
   (a) at least one saturated carbon atom containing ring having at least 6 member atoms or
   (b) an acyclic structure in which there are at least 3 quaternary carbon atoms, and

(3) having a coefficient of traction of at least 0.06 as measured by thrust-bearing test machine.

Thus the tractive fluids include the cycloalkanes, saturated heterocyclics, hydrocarbon-substituted cycloalkanes, oxygen - containing substituted cycloalkanes, certain esters, and certain oligomers of saturated carbon - containing rings.

A non-exclusive list of particularly preferred tractants includes the following. (The prefix "x" indicates that the substituents so designated may occupy any of the available positions in the ring to which it is attached). Isodecylcyclohexane, isopentadecylcyclohexane, cyclododecane, bicyclohexyl, alkyl bicyclohexyls for example 4 - (1 - methylethyl)bicyclohexyl, 4,4′ - bis(1 - methylethyl)bicyclohexyl, and x-isohexyl - 4′ - isopropyl - bicyclohexyl, x-cyclopentylbicyclohexyl, dicyclohexylmethane, (x - ethylcyclohexyl)cyclohexylmethane, [x-cyclohexyl(1 - methylethyl)]cyclohexylmethane, bis(2,4,6 - trimethylcyclohexyl)-methane, 1,1 - dicyclohexylethane, 1,1,3 - tricyclohexylpropane, trimethylolpropane tricyclohexane - carboxylate, tercyclohexyls such as 1,2 - tercyclohexyl and 1,3 - tercyclohexyl, alkyl tercyclohexyls for example x-(1,1 - dimethylbutyl) - 1,3 - tercyclohexyl, x-(1,1 - dimethylbutyl) - 1,2 - tercyclohexyl, 1,2-isopropyltercyclohexyl and 1,3 - isopropyltercyclohexyl, bis(1,3 - cyclohexyl) - cyclohexane, 1,x - bis(methylcyclohexyl) - cyclohexane, dicyclohexyl cyclohexane - 1,3 - dicarboxylate quatercyclohexyls such as x,x′-quatercyclohexyl, quinquicyclohexyls, 6-ethyl - 2,2,4,4,11,11,13,13 - octamethyltetradecane and 2,2,4,4,13,13,15,15 - octamethylhexadecane, tricyclohexylmethane, N - cyclohexylpiperidine, neopentyl glycol dineotridecanoate, bicyclooctyl, bicyclododecyl, cyclohexyl cyclododecane, cycloheptyl cyclohexanecarboxylate, cyclooctyl cyclohexanecarboxylate, cyclododecyl cyclohexanecarboxylate, bis cis and trans 1,2 - cyclohexyl cyclohexanedicarboxylate, 1,1 - dicyclohexyl - 2 - methylpropane, 1,1 - dicyclohexyl - 2 - methylbutane, 1,1 - dicyclohexyl - 2,5 - dimethylhexane, 1,1-dicyclohexylpentane, 1,2 - dicyclohexylpropane, 1,2 - di(x - ethylcyclohexyl)propane, 2,2-dicyclohexylpropane, 2,3 - dicyclohexyl - 2,3-dimethylbutane, 1,3 - dicyclohexyl - 2 - methylbutane, 1,3-dicyclohexylbutane, 1,2,3-tricyclohexylpropane, and cyclopentamethylene dicyclohexylsilane.

Mixtures of such compounds can be used and a preferred base stock for use in the compositions of the present invention is a mixture of bicyclohexyl, tercyclohexyls and 2,3-dicyclohexyl - 2,3 - dimethylbutane.

Other suitable and useful tractive fluids as defined in Specification No. 1,190,836 are those organic compounds which have from 2 to 9, fused, saturated, carbon-containing rings and have from 9 to 60 carbon atoms per molecule up to 8 of which can be replaced by atoms other than carbon atoms such as oxygen, nitrogen, phosphorus or silicon.

A comprehensive discussion of suitable fused ring compounds is provided in the reference patent, and most meet the requirement of the present invention that the compound should exhibit a coefficient of traction of at least 0.06 as measured by the thrust-bearing test machine. Preferred compounds suitable for use in the present invention include cis - decalin, cis - and trans - decalin, 2,3 - dimethyldecalin, isopropyldecalin, t - butyldecalin, perhydrofluorene, perhydrophenanthrene, perhydromethylcyclopentadiene (trimer), perhydrofluoranthene, 1 - cyclohexyl - 1,3,3 - trimethylhydrindane, x - hexylperhydrofluoranthene, x - cyclohexylperhydrofluoranthene, poly-(ethyl - 1 - methyl) - perhydrofluoranthene, x-isopropylperhydrofluoranthene, perhydrofluorene - x - cyclohexyl, perhydrofluorene-x - isododecyl, 1 - cyclohexyldecalin, 2 - (cyclohexyl - x - methyl) bicyclo(2,2,1)heptane, perhydropyrene, ethylperhydrofluorene, perhydroanthracene, bis - 2 - decalin, 1,2′-dihydrindane, perhydrocyclopentadiene trimer, 1 - cyclohexyldecalin, 2 - cyclohexyldecalin, dimethyl cyclohexyldecalin, and 4,5 - methyleneperhydrophenanthrene.

As evident from the above list of tractants, the useful fused ring compounds can be either substituted or unsubstituted. The substituents can be for instance alkyl or alicyclic hydrocarbon groups or heterocyclic carbon-containing ring structures. An alkyl substitutent can be either straight chain or branched, and can contain for example from 1 to 18 carbon atoms. When more than one alkyl substituent is present, the total number of carbon atoms in all the alkyl substituents preferably does not exceed 18.

Particularly preferred instances of base fluids of this type are decalin, cyclohexyldecalins, and alkyl substituted decalins and cyclohexyldecalins wherein the alkyl substituent or substituents contain from 1 to 18 carbon atoms. Mixtures of compounds of the above-described types may also be used as base stocks in the compositions of the invention.

In the present invention, the load-carrying or antiwear properties of the tractive fluid are improved by incorporating into the fluid a zinc di(neo - alkyl)phosphorodithioate wherein the neo - alkyl group contains from 5 to about 13 carbon atoms, for example zinc

di(neo - pentyl)phosphorodithioate or zinc di-(neo - hexyl)phosphorodithioate. Other zinc di(neo - alkyl)phosphorodithioates which can be used are those wherein the neo - alkyl group is, for example, neo - heptyl, neo - octyl, neo - decyl, neo - undecyl, neo - dodecyl, or neo - tridecyl.

Although zinc dialkylphosphorodithioates generally, and zinc 2 - ethylhexyl - isopropylphosphorodithioate in particular, are known to be antiwear agents, these compounds as a class have been found to be unsuitable for use in tractant fluids because of an adverse effect on oxidation resistance as discussed below. It was therefore surprising and unexpected to find that the zinc di(neo - alkyl(phosphorodithioates and particularly zinc di(neo - hexyl)phosphorodithioate, significantly improve the load-carrying capability of the fluid without decreasing the oxidation resistance.

Thus, the normal - alkyl equivalent of the preferred additive of this invention, zinc di-(n - hexyl)phosphorodithioate, reduced the oxidation resistance of the tractant as shown by a large increase in viscosity upon exposure to oxidation. Likewise the 1,3 - dimethylbutyl compound caused a major increase in viscosity of the fluid in the oxidation test, and the isobutyl 2 - ethylhexyl and 2 - ethylhexyl isopropyl compounds each caused substantial increases in corrosivity of the fluid. On the basis of the unfavorable results obtained with these compositions, the excellent results obtained with the di(neo - alkyl) additives were not to be predicted.

In the normal practice of this invention, the zinc di(neo - alkyl) - phosphorodithioate is added to the base at a concentration of at least 0.1% by weight of the base stock, and preferably at a concentration of from 0.5 to 2% by weight. Higher concentrations can of course be used, but no substantial improvement in results is generally obtained thereby.

The compositions of the invention may also contain viscosity index improvers to meet the temperature/viscosity requirements for certain tractive drive uses, and other additives such as antioxidants, anticorrosion agents, dispersants and dyes.

In obtaining the results presented below, the coefficient of traction was determined on the "Thrust Bearing Test Machine" described in "Effect of Lubricant Composition of Friction as Measured With Thrust Ball Bearings" by F. G. Rounds [*J. Chem. and Eng. Data*, Vol. 5, No. 4, pp. 499 (1960)]. This machine measures the torque transmitted from a central drive shaft to a torque arm through two thrust ball bearings which are submerged in the test fluid. The bearings are shaft-mounted and can be rotated while being subjected to an axial thrust load. Thrust loads are applied hydraulically or by compressing calibrated Belleville springs. A tachometer geared to the drive shaft measures the rotational speed. Thermocouples located within 1/8-inch of the balls of the test bearings measures the test fluid temperature which is held constant at various predetermined temperatures by heating or cooling the jacket fluid in the housing surrounding the test chamber.

The individual balls tend to spin on an axis parallel to the principal bearing axis as well as roll around the raceway. As a result, both rolling and sliding actions contribute to the traction. The output torque is measured with the torque arm which is fitted between the two bearings. This measured torque is then interpreted in terms of coefficient of traction for the tractant being evaluated. The coefficients obtained from this test machine are relatable to those measured in actual tractive drives. Hence, the machine is effective for screening candidate fluids. In determining the coefficients of traction reported in Tables I and II below, tractant temperature was maintained at 200° F., the Hertz stress was 500,000 psi, and the linear ball velocity was 800 feet per minute.

The Oxidation and Corrosion test (O & C) was conducted according to Federal Test Method No. 791—5308.4 under the following special conditions:

Temperature	— 350° F.
Time	— 72 hours
Air	— 5 liters
Metals	— Mg, Al, Cu, Fe

The Wear Scar Test Data was obtained according to the standard Shell 4-ball test, compared with 52100 steel balls at 200° F. and 1260 rpm. under a 40 kgm. load.

The data in Table I below wherein the present invention is illustrated by Examples 2 and 3, show the advantages of zinc di(neo-alkyl)phosphorodithioates over related compounds in a typical tractant composition consisting of a mixture of dicyclohexyl, tercyclohexyl and 2,3 - dicyclohexyl - 2,3 - dimethylbutane containing 1.5 percent of an alkyl methacrylate - vinyl pyrrolidone copolymer as a viscosity index improver.

TABLE I

Example	Additive(1)	Coefficient of Traction	O & C Test		Wear Scar Test(4)
			Viscosity(2)	Copper Corrosion(3)	
1	None (Control)	0.0618	6	−0.04	0.62
2	1% di(neo-hexyl)	0.0638	13	+0.40	0.43
3	1% di(neo-pentyl)	—	5	−1.3	0.44
4	1% di(n-hexyl)	0.0629	2050	−1.03	—
5	1.2% 1,3-dimethylbutyl	—	180	−0.7	0.46
6	1% 2-ethylhexyl isopropyl	—	2344	−3.5	—
7	1% isobutyl-2-ethylhexyl	—	1800	−7.7	0.49
8	2% 2-ethylhexyl isopropyl	0.0623	24	−5.4	—

(1) Zinc (alkyl alkyl) phosphorodithioate, % by weight of base fluid.

(2) Viscosity increase at 100°F. — Specification: less than 30.

(3) Mg. metal lost/sq. cm. surface area — Specification: less than −0.6.

(4) Scar diameter — Specification: less than 0.45 mm.

The data of Table I clearly illustrate the advantages to be gained by using the zinc di-(neo - alkyl)phosphorodithioate additives of this invention. In Example 2 a preferred embodiment of this invention, the addition of zinc di(neo - hexyl) - phosphorodithioate to the base fluid of Example 1 decreased the wear scar diameter from 0.62 mm. to 0.43 mm. The small increase in viscosity of 13% during the O & C test was well within the specification set for this property. The small weight gain in the copper corrison during the O & C test is indicative of a protective deposit being formed on the metal surface. Test results and visual observations indicate that this deposit does not interfere with the function of the tractant.

A similar improvement in the wear scar test data was obtained by adding 1% zinc di(neopentyl)phosphorodithioate to the tractant composition of Example 1 as shown by the data in Example 3. In this case, however, a small increase in the copper corrosion rate during the O & C test accompanied the addition of the additive. In certain applications where a corrosion rate of this magnitude is not acceptable, it is contemplated that a copper metal deactivator can be included in the tractant formulation.

The additives of Examples 4 and 5 were unsatisfactory because of the large viscosity increases occurring during the O & C test. Examples 6, 7 and 8 show the effect of other known zinc alkylalkylphosphorodithioate load-carrying additives on the oxidation stability of the tractive fluids of this invention and further illustrate that zinc phosphorodithioate compounds as a class are not suitable additives for use in tractive fluids.

The data in Table II below illustrates the effectiveness of the preferred zinc di(neo-hexyl)phosphorodithioate additive in reducing the wear scar diameter when present in the base stock over a concentration range of from 0.1% to 1.0% by weight of the base stock. The composition of the base stock was essentially the same as that described for the tests shown in Table I.

TABLE II

Example	Concentration of Zinc di(neo-hexyl)-phosphorodithioate	Wear Scar Diameter, mm.	% Improvement
9	0	0.76	—
10	0.1	.66	13
11	0.25	.49	35
12	0.50	.43	43
13	1.0	.44	42

$$\% \text{ Improvement} = \frac{0.76 - \text{Wear Scar Diameter}}{0.76} \times 100$$

It is apparent from the above data that substantial improvement in the load-carrying capability of the fluid is obtained by the addition of as little as 0.1% of zinc di(neo-hexyl)phosphorodithioate.

WHAT WE CLAIM IS:—

1. A composition comprising (A) a major amount of a tractant base stock comprising an organic compound having a coefficient of traction of at least 0.06, and (B) an amount sufficient to improve the load-carrying capability of the base stock of a zinc di(neo-alkyl)phosphorodithioate wherein the neo-alkyl groups each contain from 5 to 13 carbon atoms.

2. A composition according to Claim 1, wherein the amount of (B) is at least 0.1% by weight of the base stock.

3. A composition according to Claim 2, wherein the amount of (B) is from 0.5 to 2% by weight of the base stock.

4. A composition according to any of Claims 1 to 3, wherein the base stock is (I) a compound having from 12 to 70 carbon atoms per molecule, up to 8 of which can be replaced by atoms other than carbon, the said compound having a structure comprising (a) at least one saturated carbon-containing ring having at least 6 member atoms, or (b) an acrylic structure in which there are at least 3 quaternary carbon atoms, (II) a saturated compound having from 2 to 9 fused rings and a carbon atom content of from 9 to 60 per molecule, up to 8 of which atoms can be replaced by atoms other than carbon, or (III) a mixture of such compounds.

5. A composition according to Claim 4, wherein the atoms other than carbon which can replace carbon atoms in the organic compound are selected from oxygen, nitrogen, phosphorus and silicon atoms.

6. A composition according to any of Claims 1 to 3, wherein the base stock is selected from bicyclohexyl, alkyl bicyclohexyls, tercyclohexyls, alkyl tercyclohexyls, quatercyclohexyls, quinquicyclohexyls, 2,3 - dicyclohexyl-2,3 - dimethylbutene, and mixtures thereof.

7. A composition according to Claim 6, wherein the base stock is a mixture of bicyclohexyl, tercyclohexyl and 2,3 - dicyclohexyl - 2,3 - dimethylbutane.

8. A composition according to any of Claims 1 to 3, wherein the base stock is selected from decalin, cyclohexyldecalins, and alkyl substituted decalins and cyclohexyldecalins wherein the alkyl contains from 1 to 18 carbon atoms.

9. A composition according to any of Claims 1 to 8, wherein (B) is zinc di(neo-pentyl)-phosphorodithioate.

10. A composition according to any of Claims 1 to 8, wherein (B) is zinc di(neo-hexyl)phosphorodithioate.

11. A composition according to any of Claims 1 to 10, that contains a viscosity index improver.

12. A composition according to Claim 1 substantially as shown in either of Examples 2 and 3.

13. A tractive drive comprising at least two relatively rotatable members in torque-transmitting relationship, the tractive surfaces of said members having disposed thereon a tractive fluid that is a composition according to any of Claims 1 to 12.

J. C. LUNT,
Chartered Patent Agent,
Monsanto House,
10—18, Victoria Street,
London, S.W.1.

Printed for Her Majesty's Stationery Office by the Courier Press, Leamington Spa, 1973.
Published by the Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from which copies may be obtained.